

Aggregation of amphiphilic polymers in the presence of adhesive small colloidal particles

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The interaction of amphiphilic polymers with small colloids, capable to reversibly stick onto the chains, is studied. Adhesive small colloids in solution are able to dynamically bind two polymer segments. This association leads to topological changes in the polymer network configurations, such as looping and cross-linking, although the reversible adhesion permits the colloid to slide along the chain backbone. Previous analyses only consider static topologies in the chain network. We show that the sliding degree of freedom ensures the dominance of small loops, over other structures, giving rise to a new perspective in the analysis of the problem. The results are applied to the analysis of the equilibrium between colloidal particles and star polymers, as well as to block copolymer micelles. The results are relevant for the reversible adsorption of silica particles onto hydrophilic polymers, used in the process of formation of mesoporous materials of the type SBA or MCM, cross-linked cyclodextrin molecules threading on the polymers and forming the structures known as polyrotaxanes. Adhesion of colloids on the corona of the latter induce micellization and growth of larger micelles as the number of colloids increases, in agreement with experimental data.

I. INTRODUCTION

The interaction between polymers and small solute molecules, such as surfactants or colloidal particles, attracts a great interest due to wide industrial applications and their biological significance^{1,2}. For example, polymers are used to control the stability of colloidal suspensions^{3,4}, block copolymer micelles are employed for targeted delivery of small colloids⁵, but essentially the interaction of biopolymers with proteins or membrane phospholipids is of fundamental importance⁶. In addition, the interactions of hydrophilic polymers and brushes with *large* colloidal particles⁷⁻⁹ or micelles¹⁰ has been a subject of intensive research.

The presence of hydrophilic polymers induces the formation of polymer-surfactant aggregates in the form of micelles covered by polymer chains¹⁰. This cooperative association usually happens below the CMC of the surfactants. Large colloidal particles form aggregates with polymers where hydrophilic polymer chains are wrapped around colloidal particles^{7,8}. The polymer chains can link different colloids between each other, thus resulting in the clustering of colloids⁹ or gel formation⁷. In turn, several polymer chains can adsorb on the same colloidal particle forming the hydrophilic corona and stabilizing it. A notable feature of such aggregates is that if adsorption is reversible, colloidal particles can effectively slide along the chain. In the case of many long chains adsorbed on the same colloidal particle, this sliding degree of freedom results in the formation of star-shaped aggregates with annealed number of arms⁷.

However, the interaction of polymers with *small* colloidal particles has received relatively little attention. In this paper we precisely focus our interest on interactions of hydrophilic polymers with *small* colloidal particles that can reversibly stick to hydrophilic parts of the polymer backbone. In contrast to large colloids, the polymers do not adsorb onto the particles but only adhere onto a few active sites, i.e., the small colloids induce topological changes in the polymer configurations, promoting looping, cross-linking, and interconnections between the chains. In this context, the following situations, which are relevant in practice, can be mentioned: (i) The driving force for the formation of mesoporous silica-based materials type SBA or MCM¹¹ is the strong interaction of hydrophilic polymers with silica particles, e.g. TEOS, and the subsequent formation of self-assembled structures. The possibility of tuning and controlling the design of the resulting structures is a challenging task. Silicon alkoxides in water form Si-OH compounds, but also different pairs or oligomers

of silicon, namely Si-O-Si¹². Silica particles form hydrogen bonds with hydrophilic polymer's backbone¹³. Since the hydrogen bonds are relatively weak, the silica particles can effectively slide along the chain by breaking and re-forming new hydrogen bonds. Thus, we can consider a silica particle as being either a sliding link between different chains or a sliding loop on the same chain. Addition of silica particles to the solution of block copolymer micelles leads to the adsorption of silica particles on the coronas of micelles¹¹. The practical example of such systems is an aqueous solution of TEOS with common triblock copolymers Pluronic P123 (EO₂₀-PO₇₀-EO₂₀) or Pluronic F127 (EO₁₀₆-PO₇₀-EO₁₀₆). The micelles and self-assembled ordered structures of these polymers serve as precursors for the pores in the mesoporous materials. The diameter of hydrophobic cores of micelles determines the size of the pores, while the structure of the polymeric corona is responsible for the microporosity of the material¹⁴. Therefore, the control of the adhesion of the silica particles into the coronas can lead to the control of the core of the micelle and, eventually to the control of the properties of the final porous material. (ii) A cone shaped molecules with a hydrophobic cavity known as cyclodextrins^{15–17} can spontaneously thread on linear hydrophilic polymers. Polymer chains dressed with necklaces of cyclodextrins bear the special name of polyrotaxanes. Since two molecules of cyclodextrins can be covalently bound together, the resulting molecule will represent two linked rings. Such molecules can either link two chains or form a loop on the same chain, providing a sliding degree of freedom for the chain to move inside the rings. In previous works the effect of these sliding links for the polymers grafted to a surface¹⁸ and the micelles with sliding coronas¹⁹ has been studied.

In this paper we introduce a formalism suitable for a qualitative description of these mentioned processes, in which flexible polymers interact with small colloidal particles or other agents, that induce binding with the polymers. A complete statistical mechanical description of these processes is of extreme complexity due to the changing topology of the system due to the adhesion of the colloids in different chain backbones and, therefore, we will here focus on the qualitative trends that a scaling theory can reveal. Formally, the complex topology of the polymeric network, produced by the presence of the binding agents as shown in Figure 1, permits us to use known results of polymeric networks of fixed topology, for which the relevant scaling exponents are known²⁰. The challenging objective of our work is thus to derive the partition function for a system where the *vertices* of the polymeric network can slide along chain backbones and, therefore, the topology of the system is not fixed. This

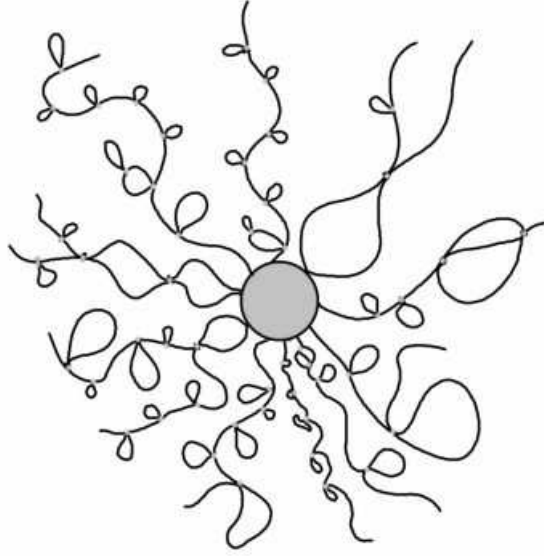


FIG. 1. Schematic representation of a block copolymer micelle with small colloids in the corona. This sketch shows possible topologies addressed in this work.

is precisely the case of the physical situations that we have described so far, and that cannot be trivially addressed by a simple mapping of the fixed topology results, as done in other context^{21–23}. An important consequence of this fact is that, in the integration of this degree of freedom, the system passes through regions with different topology, characterized by different sets of scaling exponents. In the next section we present what, to the best of our knowledge, is the first derivation of this effect. Therefore, in the following we formulate our scaling model and address the question of the calculation of the singular non-trivial contribution to the entropy of a system of hydrophilic polymers with small colloidal particles forming different mobile polymer architectures. With the construction of this singular part of the partition functions, according to the scaling theory, we find the most favorable conformations of the system and, as a consequence, the distribution of colloids along the chains, for instance.

Within this formalism we can calculate the regimes of loading of silica particles in linear polymers, star polymers, and in micelles of block copolymers, and permits us to give a theoretical justification of several experimentally observed facts. We believe that our approach can be useful in biophysical applications in systems like DNA chains interacting with proteins related to gene regulation models, where equilibrium analyses have been carried out²⁴, and also the effect of looping on the transport of proteins along the chain

has been analyzed^{25,26}. Related analyses can be carried out to study the problem of DNA denaturation²⁷ and, effectively, have been done to study the equilibrium shapes of knots in chains^{28,29}.

The paper is organized as follows. In section II, we introduce the model of the system and perform the scaling analysis. Section III is devoted to the study of the equilibrium between polymeric systems and colloidal particles, in particular, colloids with star polymers and colloids with block copolymer micelles. Finally, section V is devoted to the conclusions that we have drawn from this work.

II. MODEL

In this section we propose the scaling form of the partition function for systems, polymeric networks, of different topology. Such a partition function contains a trivial energetic contribution arisen from the short-range interaction between the binding agents and polymer segments. However, the entropic contribution strongly depends on the topology of the polymeric network resulting from that interaction, together with the topological effects that are related to the topology of the polymer itself, as in the case of star polymers. To that purpose, we refer to the results obtained by Duplantier^{20,30}, for the partition function of polymer networks of arbitrary topology. Such a partition function has a superscaling form $Z \sim s^N N^{\gamma_{\mathcal{L}}-1} g(n_1/N, n_2/N, \dots, n_k/N)$, where N is the total length (total number of monomers) of a network, s is a non-universal geometrical constant, n_1, \dots, n_k are the lengths of different polymeric threads between two crosslinks, or between a crosslink and a dangling end, such that $\sum n_j = N$, and g is an unknown function. $\gamma_{\mathcal{L}}$ is the universal exponent which does not depend on the type of interactions and is determined only by the topology of the system. It is given by²⁰

$$\gamma_{\mathcal{L}} - 1 = -d\nu q_{loop} + \sum_{k \geq 1} p_k \sigma_k \quad (1)$$

where q_{loop} is the number of independent loops, p_k is the number of vertices with k legs, d is the dimension of the space, ν is the Flory exponent, associated to the radius of gyration of a self-avoiding walk, σ_k is the exponent corresponding to a vertex with k -legs. The universal exponents ν and σ_k are known exactly for $d = 2$ and $d \geq 4$ and numerically for $d = 3$. In the following we use the values of σ_k obtained from the simulation results for critical exponents of star polymers³¹. Although a general form of the function $g(n_1/N, n_2/N, \dots, n_k/N)$ is

not analytically known, the scaling behavior of the system can be derived from the scaling form of g when some of its arguments go either to 0 or to 1. This scaling form gives the correct asymptotes in these limiting cases. Due to the fact that our interest lies only in the derivation of the scaling behavior of the overall system, we will avoid the explicit construction of the crossover functions between different regimes, characterized by different topologies, by basically assuming that the crossover function is of the order of a constant and matching these constants at the crossover region between different topologies, as shown shortly. This method allows us to derive an approximate description over the whole range of topological configurations of the system. From a physical point of view N as well as series of n_1, n_2, \dots , representing the size of the branches of the polymer network represent the number of Kuhn segments of each polymeric thread. Furthermore, the validity of the scaling analysis is restricted to a system with N being very large. In particular, Monte Carlo simulations on isolated polymers^{32,33} indicate that the scaling limit is reached for sizes exceeding hundreds of Kuhn segments, and therefore our analysis will be restricted to polymeric systems of at least this size. With regard to the colloidal particle, we will consider that its size is slightly larger than the Kuhn segment but much smaller than the overall size of the polymeric network.

We base our model on the following assumptions regarding the polymer–small colloids interactions: (i) one sliding sticker can bound several polymer units either on the same chain or different chains; (ii) the links are reversible and, hence, the reversibility allows for an effective sliding of the sticker along the chain; (iii) we assume steric repulsion between small colloids. Then the colloids and polymers bind together they define a network whose topology can change due to the sliding degree of freedom of the colloid. It is important to realize, however, that the *sliding* can physically take place by reversibly breaking and reforming bonds between the polymer and the colloid, regardless whether the colloid completely unbinds from the chain or it slides from site to site, since both are dynamic processes whose effect is accounted for by the equilibrium statistical mechanical treatment. Hence the challenging objective of this work is to determine the partition function of a system with fixed number of polymers and binding agents, taking into account the degree of freedom of the motion of the colloid along the chain backbone and, at the same time, correctly accounting for the topological changes in the network originated by this degree of freedom. Up to the best of our knowledge, this task has not been carried out up to date.

TABLE I. Numerical values of the critical exponent ν and star exponents σ , obtained by interpolation of Monte Carlo results for star polymers³¹ in $d = 3$ dimensions.

| $d\nu$ | σ_1 | σ_2 | σ_3 | σ_4 | σ_5 | σ_6 | σ_7 | σ_8 | σ_9 |
|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1.776 | 0.079 | 0 | -0.193 | -0.479 | -0.849 | -1.292 | -1.803 | -2.377 | -3.014 |
| σ_{10} | σ_{11} | σ_{12} | σ_{13} | σ_{14} | σ_{15} | σ_{16} | σ_{17} | σ_{18} | σ_{19} |
| -3.709 | -4.449 | -5.240 | -6.084 | -6.975 | -7.916 | -8.898 | -9.926 | -10.991 | -12.093 |

In what follows we will apply the formalism to systems of increasing complexity, emphasizing the details of the calculations in the simpler systems and making the extension to more complex systems.

A. Stickers in linear chains

Let us first examine the case of an isolated chain with a single sliding sticker binding two Kuhn segments, as shown in Figure 2. In this figure, one can identify one crosslink and two chain ends, which divide the chain into three threads. If the chain has a total length N , the first thread is a tail of size l , the second is a loop of size n , and then another tail of length $N - n - l$.

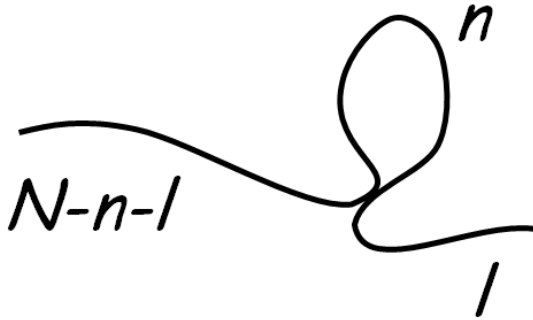


FIG. 2. A single loop of n monomers created by a sticker at a distance l from one of the ends.

The partition function of the structure sketched in Figure 2, has a general form $Z \sim s^N N^{\gamma_{\mathcal{L}}-1} g(l/N, n/N, (N-l-n)/N)$, where the exponent is given by eq. (1), with $q_{loop} = 1$, with two vertices of one leg σ_1 , and one vertex of four legs σ_4 , i.e. $\gamma_{\mathcal{L}} - 1 = 2\sigma_1 + \sigma_4 - d\nu$ (see Table I for numerical values). Without the explicit knowledge of the crossover function g , the exact partition function for the system of Figure 2, with the sliding degree of freedom,

cannot be obtained. However the scaling behavior can be derived from the singular form of g in the appropriate limit, obtained by making some of its arguments going to 0 or to 1, where g is expected to behave either as a power law or as a constant. With this in mind, we propose a power law form of the partition function that will permit us to properly interpolate between the singular behavior of the crossover function g in the different limits, i.e.

$$Z \sim n^x l^y (N - n - l)^z \quad (2)$$

where the exponents x, y, z can be fixed from the known limits. In this simple case, one of these limits is, for example, $l/N \rightarrow 0$, $n/N \sim 1$, and $(N - n - l)/N \sim 1$. Our procedure will become apparent in what follows.

The partition function of the system requires the integration over the sliding degree of freedom. The final result has a general structure of the form

$$Z(N, m) \sim e^{-m\varepsilon/kT} s^N \tilde{Z}(N, m) \quad (3)$$

where m is the number of stuck colloids, and the factor $e^{-m\varepsilon/kT}$ takes into account the interaction energy in the sticking process. The entropic part contains the trivial factor s^N depending only on the number of monomers contained in the polymeric network. \tilde{Z} takes into account the nontrivial contribution to the configurational part of the partition function which depends on the topology of the polymeric network, but also on that induced by the presence of m colloids adhered to the polymer. From now on, we will concentrate on \tilde{Z} , and omit the tilde, for the ease of notation, where confusion could not occur.

For the case of one polymer chain and one colloid, the nontrivial part of the partition function takes the form

$$Z(N, m = 1) \sim 2 \int_0^{N/2} dl \int_0^{N-2l} dn g(l/N, n/N, (N - l - n)/N) \quad (4)$$

The integration limits take into account that the system is invariant under the permutation of the two tails and therefore we can restrain the integration domain by the line $l = (N - n)/2$, which implies that the tail of size l is the smallest tail. We have to further split the integration domain into separate regions of different topologies due to the fact that each topology requires a set of exponents x, y, z in equation (2) to consistently interpolate between the appropriate limits. We can argue that these regions are characterized by I) small loop,

$n < l < N-l-n$, II) intermediate loop, $l < n < N-l-n$; and III) big loop, $l < N-l-n < n$. Due to the fact that we take l as the smallest tail without loss of generality. We then have

$$\begin{aligned}
Z(N, m=1) &\sim \int_0^{N/3} dl \int_0^l dn n^x l^y (N-n-l)^z + \int_{N/3}^{N/2} dl \int_0^{N-2l} dn n^x l^y (N-n-l)^z \\
&+ C_1 \int_0^{N/3} dn \int_0^n dl n^{x'} l^{y'} (N-n-l)^{z'} \\
&+ C_1 \int_{N/3}^{N/2} dn \int_0^{N-2n} dl n^{x'} l^{y'} (N-n-l)^{z'} \\
&+ C_2 \int_{N/3}^{N/2} dn \int_{N-2n}^{(N-n)/2} dl n^{x''} l^{y''} (N-n-l)^{z''} \\
&+ C_2 \int_{N/2}^N dn \int_0^{(N-n)/2} dl n^{x''} l^{y''} (N-n-l)^{z''}
\end{aligned} \tag{5}$$

where the constants C_1 and C_2 measure the relative weight between the functional form taken for each of the contributions. In what follows we will determine the three sets of exponents and evaluate the contributions of each term to the partition function.

II) Intermediate loop, $l < n$. In this region, only three limits are possible. In the first limit we consider that all legs and the loop are of a similar size and of order N . Therefore, according to eq. (2), $Z \sim N^{x'+y'+z'}$. Then, making use of the general expression for the topological exponents given in equation (1), one can write

$$x' + y' + z' = 2\sigma_1 + \sigma_4 - d\nu \tag{6}$$

corresponding to a topology of two free ends at the extremes of the two tails, plus a vertex of four legs where the loop closes in the middle of the polymer. In the second limit, if the small tail vanishes, $l \rightarrow 1$ ($l/N \rightarrow 0$) with $n \sim N/2$ and $(N-n-1) \sim N/2$, the topology of the system evolves towards a long tail with the loop at the end, characterized by a topology with the presence of one free end at the extreme of the remaining long tail, and a vertex of three legs for the loop closed at the other end of the tail. Then $Z \sim n^{x'} 1^{y'} (N-n)^{z'}$. Since this expression has to be compatible with the known singular behavior of the system with the mentioned topology (1), we further have

$$x' + z' = \sigma_1 + \sigma_3 - d\nu \tag{7}$$

Finally, in the third limit, if both, the small tail and the loop, vanish, $l < n \rightarrow 1$, we get a free chain topology and thus

$$z' = 2\sigma_1 \quad (8)$$

These three equations permit us to find the numerical value of the desired exponents for the interpolating function that will be used in the integration to derive the singular behavior of the partition function. We obtain $x' = \sigma_3 - \sigma_1 - d\nu$, $y' = \sigma_1 + \sigma_4 - \sigma_3$, and $z' = 2\sigma_1$.

We can now write the partition function of this domain in the form of nested integrals

$$\begin{aligned} Z_{II} \sim & \int_0^{N/3} dn n^{\sigma_3 - \sigma_1 - d\nu} \int_0^n dl l^{\sigma_1 + \sigma_4 - \sigma_3} (N - n - l)^{2\sigma_1} + \\ & + \int_{N/3}^{N/2} dn n^{\sigma_3 - \sigma_1 - d\nu} \int_0^{N-2n} dl l^{\sigma_1 + \sigma_4 - \sigma_3} (N - n - l)^{2\sigma_1} \end{aligned} \quad (9)$$

In both terms, since $\sigma_1 + \sigma_4 - \sigma_3 \approx -0.2 > -1$ and $2\sigma_1 = 0.16 > 1^{34}$, the inner integral converges. However, the inner integral in the first contribution behaves as $n^{\sigma_1 + \sigma_4 - \sigma_3 + 1}$ for small n . Therefore the outer integral is diverging due to lower bound, leading to a contribution of the order $\Delta^{\sigma_4 - d\nu + 2} N^{2\sigma_1} \approx \Delta^{\sigma_4 - d\nu + 2} N^{0.16}$, where Δ is the lower cutoff for the size of the loop, of the order of one monomer. The second contribution is convergent, yielding $N^{\sigma_4 - d\nu + 2\sigma_1 + 2} \int_{1/3}^{1/2} dt t^{\sigma_3 - \sigma_1 - d\nu} \int_0^{1-2t} ds s^{\sigma_1 + \sigma_4 - \sigma_3} (1 - t - s)^{2\sigma_1} = 0.31 N^{\sigma_4 - d\nu + 2\sigma_1 + 2} \approx 0.31 N^{-0.098}$. Therefore, in the limit $N \rightarrow \infty$ the partition function is dominated by the first term

$$Z_{II} \sim \Delta^{\sigma_4 - d\nu + 2} N^{2\sigma_1} \quad (10)$$

This result indicates that big loops are not entropically favorable and that the system will tend to reduce the size of the loop to the minimum. Moreover, since in this limit the small tail is, by construction, smaller than the loop, the most probable conformation is hence a minimal loop at the end of a long tail.

I) To evaluate Z_I , one has to consider that the loop is smaller than the shortest tail, $n < l$. When the sizes of the loop and the tails are comparable, we have the same scaling as in the II-part. Hence, in the latter case

$$x + y + z = 2\sigma_1 + \sigma_4 - d\nu \quad (11)$$

Notice that when the loop and the tails are comparable and of the order of N , the integrands of the II- and I- part should be comparable. Since the functional form is also the same for both cases, we have that the constant $C_1 \sim 1$.

As before, to fix the exponents we identify the singular limits compatible with the condition $n < l$. Taking $n \rightarrow 1$, the free chain limit is recovered and hence

$$y + z = 2\sigma_1 \quad (12)$$

Furthermore, when the small tail vanishes, this implies a simultaneous vanishing of both the loop and the tail, $n < l \rightarrow 1$. One gets

$$z = 2\sigma_1 \quad (13)$$

Finally, one also obtains $x = \sigma_4 - d\nu$, $y = 0$. The partition function reads

$$Z_I \sim \int_0^{N/3} dl \int_0^l dnn^{\sigma_4 - d\nu} (N - n - l)^{2\sigma_1} + \int_{N/3}^{N/2} dl \int_0^{N-2l} dnn^{\sigma_4 - d\nu} (N - n - l)^{2\sigma_1} \quad (14)$$

Since again the integrand of the inner integrals diverge the integral is dominated by $n \rightarrow \Delta$. The outer integrals have a regular integrand and the whole term scales as $N^{2\sigma_1+1}$. Then the final expression for the partition function of this part is

$$Z_I \sim \Delta^{\sigma_4 - d\nu + 1} N^{2\sigma_1 + 1} \quad (15)$$

This partition function indicates that under the condition $n < l$ the most favorable conformation is the existence of a minimal loop traveling along the chain. Notice that this contribution has an extra N factor as compared to the case II, that is $Z_I/Z_{II} \sim N/\Delta \rightarrow \infty$, for very long chains, indicating that this contribution will be dominant. Similar conclusion is drawn for the case knots in chains³⁵.

III) The third contribution in (5) is obtained as before. For this case the relevant limits are: both tails and the loop are of the same order, one tail vanishes, $l \rightarrow 1$, both tails tend to vanish $l < N - l - n \rightarrow 1$. With these limits we find $x'' = -d\nu$, $y'' = \sigma_1 + \sigma_4 - \sigma_3$, and $z'' = \sigma_1 + \sigma_3$. Furthermore, since Z_{III} should be comparable with Z_I and Z_{II} when the two tails are of the same order we conclude that C_2 is of order 1.

$$\begin{aligned}
Z_{III} \sim & \int_{N/2}^N dn \int_0^{(N-n)/2} dl n^{-d\nu} l^{\sigma_1+\sigma_4-\sigma_3} (N-n-l)^{\sigma_1+\sigma_3} + \\
& \int_{N/3}^{N/2} dn \int_{N-2n}^{(N-n)/2} dl n^{-d\nu} l^{\sigma_1+\sigma_4-\sigma_3} (N-n-l)^{\sigma_1+\sigma_3}
\end{aligned} \tag{16}$$

Both integrands have integrable divergences and, therefore, the N dependence of Z_{III} can be trivially obtained as before $N^{\sigma_4-d\nu+2\sigma_1+2} \left[\int_{1/2}^1 dt t^{-d\nu} \int_0^{(1-t)/2} ds s^{\sigma_1+\sigma_4-\sigma_3} (1-t-s)^{\sigma_1+\sigma_3} + \int_{1/3}^{1/2} dt t^{-d\nu} \int_{1-2t}^{(1-t)/2} ds s^{\sigma_1+\sigma_4-\sigma_3} (1-t-s)^{\sigma_1+\sigma_3} \right] \sim 0.44 N^{\sigma_4-d\nu+2\sigma_1+2}$

We can then conclude that the dominant contribution to the partition function of a sticker in a free chain is given by $Z \sim Z_I \sim \Delta^{\sigma_4-d\nu+1} N^{2\sigma_1+1}$, since $Z_{II}/Z_I \sim N^{-1}$ and $Z_{III}/Z_I \sim N^{\sigma_4-d\nu+1}/\Delta^{\sigma_4-d\nu+1} \sim N^{-1.26}$.

Therefore the overall N -dependence of the partition function is that of a bare chain with an extra power of N that takes into account the freedom of the location of the small loop along the chain. The loop cut-off size Δ could be linked to the local stiffness of the chain (persistence length). The optimal configuration is a small loop freely sliding along a linear chain. This is a general result and, as we describe later, is applicable to the loops sliding in the corona of a micelle or the arm of a star polymer. The position of the loop l does not enter the final expression and the distribution of positions of the small loop along the chain and hence the probability of finding the loop (the sticker) at a position l along the chain backbone $P(l)$ is uniform up to a distance Δ from the chain ends.

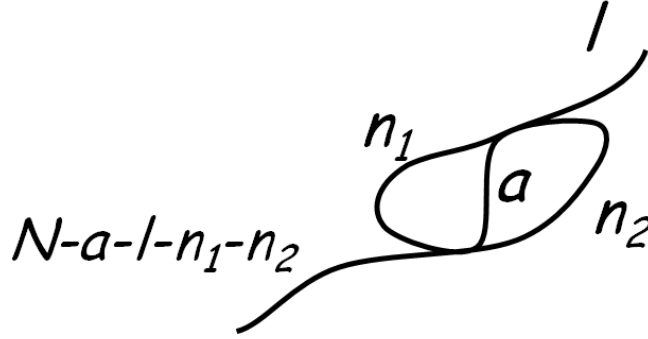


FIG. 3. Ailed loop created by two stickers on the same chain.

To end this section, let us consider the case of m stickers in one linear chain to the light of the results that we have just derived. As we have seen, the more important contribution to

the partition function is the degree of freedom of each small loop along the chain backbone. This contribution is lost if the loop becomes large as well as in conformations in which loop-like structures are linked by a sticker. For example, in ailed loops (Figure 3) the translational entropy gives a factor N while, if the loops were independent, the entropy would be of order N^2 (see Appendix A). Then the partition function for a system of m stickers in a free chain can be straightforwardly generalized considering the independent contributions of the individual loops, provided that $m\Delta \ll N$. Thus, from the expression (15) one obtains

$$Z \sim \Delta^{m(\sigma_4 - d\nu + 1)} N^m N^{2\sigma_1} \quad (17)$$

Notice that the factor $N^{2\sigma_1}$ stands for the entropy of the supporting chain. The result given in eq. (17) is only valid in the case that the sticker-sticker interactions are negligible and therefore, when the chain is not saturated.

B. Stickers in star polymers

In the following, let us assume that the star polymer has p arms, each of length N . We will proceed by analyzing the dominant diagrams starting with one colloid and then generalizing the result to an arbitrary number m of stickers adhered to the arms of the polymer as before.

1. One loop on one arm

The simplest case is that of one loop in one of the arms of the star polymer, as shown in Figure 4. The main difference with the respect to previous analysis is here the presence of the topological constraints at the vertex where the p arms meet, giving strong excluded volume interactions in the vicinity. This is reflected in the partition function of the system by the presence of highly negative exponent σ_p corresponding to strong excluded volume effects in the center.

Denoting the size of the loop by n and the distance of the loop from the center by l , we write the partition function of the system star polymer – colloid under the interpolating form already used $Z \sim n^x l^y (N - n - l)^z$, where x , y and z are exponents to be determined by matching the appropriate limits. Furthermore, as before, the set of exponents is not unique

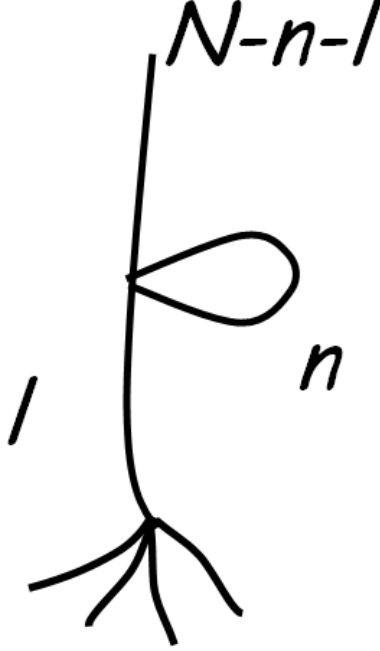


FIG. 4. Sliding loop of size n on the arm of a micelle at the distance l from the center.

but depends on the relative sizes of the three entities in which we have divided the chain, i.e. loop, tail, and distance to the vertex. We demand that these different expressions for the interpolating function continuously crossover at the limits of their validity.

Following the same analysis of the previous section, the interpolating function have to be split into six different sets of exponents due to lack of symmetry of this case. However, we know that the partition function is going to be dominated by a small loop traveling along the arm. To simplify our analysis we will concentrate on the scaling form of this regime, defined by a set of exponents in the region $n < l < N - n - l$, and a different set in the region $n < N - n - l < l$. After analyzing all the corresponding limits, one has

$$\begin{aligned}
 Z \sim & \int_0^{N/3} dl \int_0^l dnn^{\sigma_4-d\nu} (N-n-l)^{\sigma_p+p\sigma_1} + \int_{N/3}^{N/2} dl \int_0^{N-2l} dnn^{\sigma_4-d\nu} (N-n-l)^{\sigma_p+p\sigma_1} \\
 & + \int_{N/3}^{N/2} dl \int_{N-2l}^{(N-l)/2} dnn^{\sigma_4-d\nu} l^{\sigma_p+p\sigma_1} + \int_{N/2}^N dl \int_0^{(N-l)/2} dnn^{\sigma_4-d\nu} l^{\sigma_p+p\sigma_1}
 \end{aligned} \tag{18}$$

As expected, the inner integrals diverge for this small loop case when $n \rightarrow \Delta$, which reflects the aforementioned dominance of small loops with respect to large loops. After integration we get that the dominant contribution scales as

$$Z \sim \Delta^{\sigma_4 - d\nu + 1} N^{\sigma_p + p\sigma_1} N \quad (19)$$

The term $N^{\sigma_p + p\sigma_1}$ is the partition function of a star polymer of p arms, while the additional N factor stands for the translational entropy of the sliding small loop. The other topologies that we have not explicitly analyzed imply either a loop of order N or small loops that are interacting with the vertices. In all these cases the translational entropy of the loop is lost and these contributions are therefore subdominant. The integrand in the partition function (18), upon integration over n , allows us to derive the distribution of these small loops along the chain, giving

$$P(l) \sim \begin{cases} (N - l)^{\sigma_p + p\sigma_1}, & 0 < l < N/2 \\ l^{\sigma_p + p\sigma_1}, & N/2 < l < N \end{cases} \quad (20)$$

which indicates a slight repulsion of the small loop from the center of the star.

2. *Several loops on the same arm*

The partition function of several loops on the same arm can be obtained by a straightforward generalization of the previous result, as we have done for the single chain case. We obtain

$$Z \sim \Delta^{m(\sigma_4 - d\nu + 1)} N^m N^{\sigma_p + p\sigma_1} \quad (21)$$

which basically contains the bare entropy of the star polymer together with N^m factor due to the translational entropy of m loops. We have implicitly considered that the number of monomers in the i^{th} -branch, n_i is of order N . This result is however limited to the case $m\Delta \ll N$, due to the fact that no interactions between loops has been considered.

This result can be further generalized to the case where the m stickers are distributed among p branches. Let us consider a star polymer with p -arms of n_1, n_2, \dots, n_p monomers each, with $\sum_{i=1}^p n_i = N$, where colloidal particles can adhere from a given bulk solution. The complete partition function of m colloids attached to this polymer is given by

$$Z(m) \propto \sum_{m_1 + m_2 + \dots + m_p = m} e^{-m\varepsilon/kT} s^N \Delta^{m(\sigma_4 - d\nu + 1)} N^m \left(\frac{n_1}{N}\right)^{m_1} \left(\frac{n_2}{N}\right)^{m_2} \dots \left(\frac{n_p}{N}\right)^{m_p} N^{\sigma_p + p\sigma_1} \quad (22)$$

where use has been made of eq. (21) to introduce the dominant contribution to the entropy of the system, and $\sum_{i=1}^p m_i = m$. Branches are assumed to be discernable due to polydispersity considerations. However, if the size of the branches n_i are comparable and $n_i \sim N$ $n_1/N \simeq n_2/N \simeq \dots \simeq n_p/N$ we can approximately write

$$Z(m) \propto \frac{(m+p-1)!}{m!(p-1)!} e^{-m\varepsilon/kT} s^N \Delta^{m(\sigma_4-d\nu+1)} \left(\frac{N}{p}\right)^m N^{\sigma_p+p\sigma_1} \quad (23)$$

The combinatorial factor stands for all combinations of m_1, m_2, \dots, m_p such that its sum gives m .

3. m stickers looping in many arms

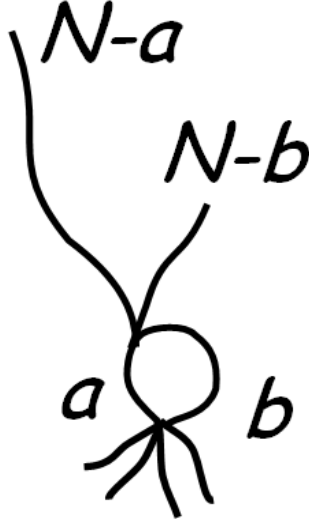


FIG. 5. A loop between two arms of a micelle created by one sticker in the center of the micelle.

The exact consideration of the general case is a formidable task in view of the multiplicity of exponents and integration domains that we have shown in the simple cases analyzed above. However, we prove here that when two arms are connected by one sticker, there is a significant entropy reduction with respect to the case where the sticker form one loop in one arm. Therefore, the dominant configuration for the general case is that in which the m stickers form small traveling loops in individual arms. To prove this, let us first consider a loop formed by two different arms as shown in Figure 5. The sticker splits a first chain into a segment a close to the center and a free tail $N - a$. The second chain is split into a segment

b and a free tail $N - b$, while the loop size is $n = a + b$. Since two arms are symmetrical we sort the tails by their respective lengths, $a < b$ this leads to $N - b < N - a$. The general form of the partition function is

$$Z \sim a^{x_1} a^{x_2} (N - a)^{z_1} (N - b)^{z_2} \quad (24)$$

where the exponents x_1, x_2, z_1, z_2 are fixed by the limits. The dominant contribution to the partition function is found in the limit $a < b < N - b < N - a$. This can be intuitively understood by noticing that the size of the loop is directly related to the location of the sticker. In this way, when the sticker is located near the chain end (a large loop) there is a strong entropy reduction due to the reduction of the two tails to create a big loop. Hence, the dominant contribution is that of a small loop near the core of the star. This argument also indicates that the translational entropy of the small loop discussed in the previous cases is here lost. Therefore the dominant contribution to the partition function reads

$$Z \sim \int_0^{N/2} db b^{\sigma_{p+2}-\sigma_p-d\nu} \int_0^b da a^{\sigma_p-\sigma_{p+2}+\sigma_4} (N - a)^{z_1} (N - b)^{z_2} \quad (25)$$

where use has been made of the relevant limits to fix the exponents, with $z_1 + z_2 = \sigma_p + p\sigma_1$ as imposed by the limit $a, b \rightarrow 0$. Since $\sigma_p - \sigma_{p+2} + \sigma_4 > -1$, the inner integral converges, giving, $Z \sim \int_0^{N/2} db b^{\sigma_4-d\nu+1} N^{\sigma_p+p\sigma_1}$, while this integral diverges on the lower limit Δ , since $\sigma_{p+2} - \sigma_p - d\nu < -1$ for all p . One finally obtains

$$Z \sim \Delta^{\sigma_4-d\nu+2} N^{\sigma_p+p\sigma_1} \quad (26)$$

Similar arguments lead to the conclusion that a larger number of loops between two different arms or nested loops of several arms as shown in Figure 6 will degenerate into immobile loop in the center: lower limit exponent < -1 for any p , including $p = 4$, and the nested integral in (25) is of order of b regardless the integrated function.

III. EQUILIBRIUM BETWEEN COLLOIDAL STICKERS AND A p -ARMED STAR

With the help of the results obtained so far we analyze here the equilibrium between a solution of small colloidal particles and polymeric structures. This method can be applied to

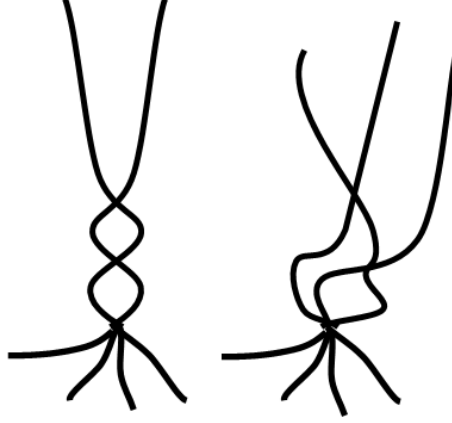


FIG. 6. Two examples of nested loops formed by two stickers in the arm of a micelle.

determine the partition function of a system in which small colloids can adhere to polymers of complex topology. On one hand, it is useful to find how the topological constraints can modify the preferred location of the colloids in the system, but also how colloids can induce the binding of different branches. Therefore, it is not a priori evident the final equilibrium structure.

In the first place, we study the case of a star polymer of p -arms in equilibrium with a suspension of colloids. In the second place, we will drive our attention to the case of block copolymer micelles, where the equilibrium can change the properties of the micelle as such. This latter case is of interest in the moulding of porous materials from the self-assembly of surfactants through silica colloids associating with the corona of copolymeric micelles, as it is the case for porous materials of type SBA or MCM, for example.

Making use of eqs. (23), the grand partition function for the system then reads

$$\Xi \propto \sum_{m=0}^{\infty} e^{\mu m/kT} Z(m) \simeq s^{pL} (pL)^{\sigma_p + p\sigma_1} \sum_{m=0}^{\infty} \left[e^{\frac{\mu - \varepsilon}{kT}} \Delta^{\sigma_4 - \nu d + 1} L \right]^m \frac{(m + p - 1)!}{m!(p - 1)!} \quad (27)$$

Stirling approximation can be used if $m \gg 1$, while p can be of order 1, thus the combinatorial factor turning into $m^{p-1}/(p-1)!$. Furthermore, we have introduced the number of monomers per arm, L , so that $N = pL$. The grand-canonical potential Ω is defined as usual $\Omega = -kT \ln \Xi$. Defining $Y(\mu) \equiv e^{\frac{\mu - \varepsilon}{kT}} \Delta^{\sigma_4 - \nu d + 1} L$ one finds that the sum is converging always that $Y(\mu) < 1$. In particular, in the limit $Y(\mu) \rightarrow 1$ we find

$$\Xi \propto \frac{1}{(1 - Y(\mu))^p} \quad (28)$$

Therefore, colloids saturate the star polymer when the chemical potential rises the critical value $\mu_c = \varepsilon + kT \ln(\Delta^{\sigma_4 - \nu d + 1} L)$. In particular, we find that the average number of colloids that aggregate in the star is given by

$$\langle m \rangle = \frac{\sum_{m=0}^{\infty} Y(\mu)^m m^p}{\sum_{m=0}^{\infty} Y(\mu)^m m^{p-1}} \rightarrow \frac{1}{1 - Y(\mu)} \frac{\Gamma(p+1) + \zeta(-p)}{\Gamma(p) + \zeta(1-p)} \simeq \frac{p}{1 - Y(\mu)} \quad (29)$$

where the last expression corresponds to the limit $Y \rightarrow 1^-$ and p is taken $p \geq 4$. Therefore, above the critical value of the chemical potential the star saturates and m becomes of the order of $1/\alpha \gg 1$, where α is $\Delta/N = \Delta/pL$. The quantity αm can be regarded as the fraction of polymer wrapping colloids, which tend to 1 at saturation.

The analysis of the saturated state cannot be done with the same rigorous approach developed so far. We will assume that saturation occurs because of the limitation of the available polymer for the colloids in one arm due to the presence of other colloids in the same arm, in the spirit of van der Waals equation of state. One can then approximately write $(L - m\Delta/p)^m$ instead of L^m and $(L - m\Delta/p)^{\sigma_p + p\sigma_1}$ in eq. (23), to account for the limitation of the size of the polymeric threads at fixed number m of minimal loops. This approximation will be valid always that $m\Delta \ll N$. One can finally write

$$Z(m, p) \propto \frac{m^{p-1}}{(p-1)!} e^{-m\varepsilon/kT} s^{pL} \Delta^{m(\sigma_4 - d\nu + 1)} L^m (pL)^{\sigma_p + p\sigma_1} \left(1 - m\frac{\Delta}{pL}\right)^m \left(1 - m\frac{\Delta}{pL}\right)^{\sigma_p + p\sigma_1} \quad (30)$$

The partition function can then be written as

$$\Xi \propto \sum_{m=0}^{N/\Delta} Y(\mu)^m \left(1 - \frac{m\Delta}{pL}\right)^{m + \sigma_p + p\sigma_1} m^{p-1} \quad (31)$$

Let us center our attention on the value of the sum

$$I_{p-1} \equiv \sum_{m=0}^{1/\alpha} Y(\mu)^m (1 - \alpha m)^{m + \sigma_p + p\sigma_1} m^{p-1} \quad (32)$$

in the limit $\alpha \rightarrow 0$, near the transition, $Y \rightarrow 1^\pm$. Then, the summand can be rewritten as

$$Y(\mu)^m (1 - \alpha m)^{m + \sigma_p + p\sigma_1} m^{p-1} \simeq e^{m \ln Y + (m + \sigma_p + p\sigma_1) \ln(1 - \alpha m) + (p-1) \ln m} \quad (33)$$

The exponent in the second expression can be regarded as an effective Hamiltonian

$$H(m) \equiv - (m \ln Y + (m + \sigma_p + p\sigma_1) \ln(1 - \alpha m) + (p-1) \ln m) \quad (34)$$

To analyze the stability of the system, let us calculate the saddle point m^* by demanding that

$$\left. \frac{\partial H}{\partial m} \right|_{m^*} = 0 \quad (35)$$

This gives the so-called equation of state, which reads in our case

$$\ln Y + \ln(1 - \alpha m^*) - \frac{\alpha(m^* + \sigma_p + p\sigma_1)}{1 - \alpha m^*} + \frac{p-1}{m^*} = 0 \quad (36)$$

Let us assume that near the transition, $\ln Y \ll 1$, the fraction of wrapped polymer αm^* is small. Then, from eq. (36) we obtain an estimate of the average value of m^* . To the lowest order in α we find $\ln Y - 2\alpha m^* - \alpha(\sigma_p + p\sigma_1) + (p-1)/m^* = 0$, which gives

$$m^* = \frac{\ln Y - \alpha(\sigma_p + p\sigma_1)}{4\alpha} \pm \frac{1}{4\alpha} \sqrt{8\alpha(p-1) + (\ln Y - \alpha(\sigma_p + p\sigma_1))^2} \quad (37)$$

The negative sign gives an unphysical $m^* < 0$ solution. This expression gives a crossover between values of Y smaller than 1 and values larger than 1 for finite α . The asymptotic behavior is obtained by expanding the expression for small α , in fact for $\ln Y/\sqrt{\alpha}$ larger than 1. At the crossover, $|\ln Y| \sim \alpha^{1/2}$. Therefore, if $1 > |\ln Y| > \alpha^{1/2}$ the solution reads

$$m^*_+ \simeq \frac{\ln Y}{2\alpha} + \frac{p-1}{\ln Y} - \frac{2(p-1)^2}{\ln^3 Y} \alpha + \mathcal{O}(\alpha \ln Y) \quad \text{for } Y > 1 \quad (38)$$

$$m^*_- \simeq \frac{p-1}{|\ln Y|} - \frac{2(p-1)^2}{|\ln^3 Y|} \alpha + \mathcal{O}(\alpha \ln Y) \quad \text{for } Y < 1 \quad (39)$$

For values of the control parameter $\alpha^{1/2} > |\ln Y| \geq 0$, the appropriate expansion reads for both branches

$$m^* \simeq \sqrt{\frac{p-1}{2\alpha}} - \frac{\sigma_p + p\sigma_1}{4} + \frac{\ln Y}{4\alpha} + \mathcal{O}\left(\alpha^{1/2}, \frac{\ln Y}{\alpha^{1/2}}\right) \quad (40)$$

This result indicates that the free energy is analytic through the transition and the saturation is therefore a crossover process as the chemical potential increases for finite α , due to the existence of this crossover regime $\alpha^{1/2} > |\ln Y| \geq 0$. However, the range of validity of eq. (40) decreases as $\alpha \rightarrow 0$ indicating that the behavior of m^* will become singular precisely in this limit. To further analyze the character of such singular behavior, we have to consider the limit $\ln Y \rightarrow 0$ with $|\ln Y| > \alpha^{1/2}$. The appropriate order parameter in this singular limit is the wrapped fraction of polymer, $\psi \equiv \alpha m^*$. Since for $\psi = \alpha m^*_- = 0$ for $Y < 1$ while $\psi = \alpha m^*_+ \sim \ln Y$ if $\alpha \rightarrow 0$. In addition, notice that $\alpha m^* \sim \alpha^{1/2} \rightarrow 0$ in the crossover regime, eq. (40). Let us further define $\zeta \equiv \ln Y \ll 1$. We then rewrite the effective Hamiltonian as

$$\alpha H(m) - \alpha(p-1) \ln \alpha \equiv h(\psi) = -(\psi\zeta + (\psi + \alpha(\sigma_p + p\sigma_1)) \ln(1 - \psi) + \alpha(p-1) \ln \psi) \quad (41)$$

Then, the main integral eq. (32) reads

$$I_{p-1} \simeq \frac{1}{\alpha^p} \int_0^1 d\psi e^{-\frac{h(\psi)}{\alpha}} \quad (42)$$

The saddle point analysis then yields

$$\psi_+^* \simeq \frac{\zeta}{2} + \alpha \frac{p-1}{\zeta} - \alpha^2 \frac{2(p-1)^2}{\zeta^3} + \mathcal{O}(\alpha\zeta) \quad \text{for } \zeta > 0 \quad (43)$$

$$\psi_-^* \simeq \alpha \frac{p-1}{|\zeta|} - \alpha^2 \frac{2(p-1)^2}{|\zeta|^3} + \mathcal{O}(\alpha\zeta) \rightarrow 0 \quad \text{for } \zeta < 0 \quad (44)$$

where we recall that $\zeta > \alpha^{1/2}$. Furthermore, the mean field stability of the solution requires

$$\begin{aligned} \left. \frac{\partial^2 h}{\partial \psi^2} \right|_{\psi^*} &\equiv h''(\psi^*) = \frac{2}{1-\psi^*} + \frac{\psi^* + \alpha(\sigma_p + p\sigma_1)}{(1-\psi^*)^2} + \alpha \frac{p-1}{\psi^{*2}} \simeq \\ &\alpha \frac{p-1}{\psi^{*2}} + 2 + \alpha(\sigma_p + p\sigma_1) + (3 + 2\alpha(\sigma_p + p\sigma_1))\psi^* + \mathcal{O}(\psi^*)^3 > 0 \end{aligned} \quad (45)$$

where second equality follows considering that we are near the transition and therefore $\psi \ll 1$. Notice, however, that the limit $\alpha \rightarrow 0$ has to be taken before $\psi \rightarrow 0$, i.e. before we approach the transition. Therefore, Since $h''(\psi) > 0$ in all the range of values of ψ , the mean field solution is stable. Therefore,

$$\left. \frac{\partial^2 h}{\partial \psi^2} \right|_{\psi^*} \approx 2 + 3\psi^* + \mathcal{O}(\psi^*)^3 > 0 \quad (46)$$

which is always positive, indicating the stability of the mean field solution. Near the transition, the energy is continuous and behaves as

$$h(\psi_+^*) \sim -\frac{\zeta^2}{4} \quad (47)$$

$$h(\psi_-^*) \sim -\alpha(p-1) \text{sign}(\zeta) \rightarrow 0 \quad (48)$$

The function $h''(\psi^*)$ is also continuous at $\zeta = 0$, since

$$h''(\psi_+^*) \sim 2 + \frac{3}{2}\zeta > 0 \quad (49)$$

$$h''(\psi_-^*) \sim 2 > 0 \quad (50)$$

In conclusion, for $\alpha \rightarrow 0$ at finite $|\zeta| \ll 1$ the system presents a crossover from a *non-decorated* state, $\psi_-^* = 0$, to a *decorated* state, $\psi_+^* \sim \zeta/2$, in which the polymeric threads are increasingly covered by colloids. However, it is noteworthy that the second derivative of the saddle point free energy is continuous in the transition, but we observe that the third derivative has indeed a finite jump. Therefore this behavior can be interpreted as a higher order phase transition in the sense of the old Ehrenfest classification, but not in the sense of an order – disorder, Ising-like transitions.

IV. MICELLES OF POLYMERS WITH STICKERS

Colloidal stickers can aggregate in coronas of block copolymer micelles and modify the equilibrium structure of micelles, which is precisely the relevant problem for the formation of mesoporous materials through self-assembly of block copolymers. After the discussion of the saturation transition, we address this structural problem. With this purpose, let us first construct the free energy of a micelle with p block copolymers and with m adhered colloids to consider afterwards the global equilibrium of a system of many different-sized micelles with free chains and colloids in the bulk.

Since the colloidal stickers interact only with the hydrophilic blocks forming the corona, only the corona contribution is affected by the presence of stickers and the partition function can be split into two factors, namely, the contribution due to the corona and that due to the core.

Thus, the free energy of corona F_{corona} is given by

$$F_{corona}(m, p) = -\ln Z(m, p) \quad (51)$$

where $Z(m, p)$ is given by (30) and we have explicitly shown the parameter p that will be relevant in the following discussion. Implicit in eq. (51) is the fact that the size of the hydrophilic block is much larger than that of the hydrophobic, so that the micelle can be regarded as effectively a star.

This repulsive contribution of the corona, which tends to solubilize the copolymers is balanced by the attraction of hydrophobic units in the core. The core contribution $F_{core}(p)$ can be written as

$$F_{core}(p) = 4\pi R_c^2(p)\gamma \quad (52)$$

where γ is the surface tension between the core and the solvent, being the core of size R_c . Assuming dense packing of the monomers in the core, the radius of the core composed by p block copolymers can be expressed as

$$R_c(p) = \left[v \frac{3}{4\pi} p L_c \right]^{\frac{1}{3}} \quad (53)$$

where v is the volume of a monomer, L_c is the length of the hydrophobic block. Finally, a

contribution, $F_{conf}(p)$ should be added due to the entropy reduction due to the aggregation of p chains into a micelle, yielding

$$F_{conf}(p) = (p-1) \ln \left[\frac{p}{V_{agg}e} v \right] \quad (54)$$

See Appendix B for the details. We consider that the core is compact and thus $V_{agg} \sim R_c^3$; hence $V_{agg} \sim vpL_c$.

Hence, the free energy of a micelle of p block copolymers and m stickers in the corona is the sum

$$F(m, p) = F_{corona}(m, p) + F_{core}(p) + F_{conf}(p) \quad (55)$$

where $p \geq 1$. The particular case $F(0, p)$ is the free energy of a clean (with no colloids adhered) micelle of p block copolymers, while $F(m, 1)$ is the free energy of a free chain decorated with m colloids. To establish the equilibrium, we have to further introduce the free energy of isolated colloids which read, $F_{colloid} = c_f \ln(\frac{c_f}{e} \Lambda_s^3)$, where c_f stands for the concentration of free colloids in the bulk and Λ_s^3 is the de Broglie's length of the colloid. Notice that we consider that the bulk solution of colloids is dilute and only the translational entropy is relevant. Furthermore, the concentration of free chains and micelles of any size are also sufficiently dilute as to neglect interactions among them.

Let $c(m, p)$ be the number concentration of micelles with p arms and m colloids. Hence, the total free energy of the solution containing all kinds of aggregates is

$$\begin{aligned} \frac{F}{VkT} = & \sum_{m=0}^{1/\alpha} \sum_{p=1}^{\infty} \left(c(m, p) \ln \frac{c(m, p)v}{e} + c(m, p) (F(m, p) - f_{ref}(T)) \right) + c_f \ln \frac{c_f v_s}{e} - c_f f_s(T) \\ & + \mu_0 \left(c_0 - \sum_{m=0}^{1/\alpha} \sum_{p=1}^{\infty} m c(m, p) - c_f \right) + \mu_b \left(c_b - \sum_{m=0}^{1/\alpha} \sum_{p=1}^{\infty} p c(m, p) \right) \end{aligned} \quad (56)$$

where the last two terms fix the total amount of colloids and copolymer chains in the system, respectively. V is the volume of the system, $c_0 \equiv N_0/V$ and $c_b \equiv N_b/V$, where N_0 and N_b are, respectively, the total number of colloids and copolymers in the system. Furthermore, $f_s(T)$ stands for $\ln v_s/\Lambda_s^3$. In turn, $f_{ref}(T) \equiv \ln v/\lambda^3$ (see appendix B). Minimization of this free energy with respect to $c(m, p)$ gives the equilibrium distribution of the aggregates by their size p and number of adhered colloids, m . That is,

$$vc(m, p) = (vc(0, 1))^p (v_s c_f)^m \exp(-[F(m, p) - f_{ref} - p(F(0, 1) - f_{ref}) - m(F(1, 0) - f_s)]) \quad (57)$$

where the Lagrange multipliers μ_0 and μ_b have been expressed through the concentrations of unimers of each species, c_f for free colloids and $c(0, 1)$ for free and clean block copolymers, which can be both considered as the control parameters.

To obtain the relationship between volume fractions of the species, we assume that there is no volume of mixing in the system. Then, the equilibrium distributions are given by

$$\phi(m, p) = \phi^p(0, 1) \phi_f^m \frac{N p v + m v_s}{N^p v} \times \exp[-(F(m, p) - f_{ref} - p(F(0, 1) - f_{ref}) - m(F(1, 0) - f_s))] \quad (58)$$

where $\phi(m, p)$ is the volume fraction of a micelle of p arms with its adhered m stickers, while $\phi(0, 1)$ and ϕ_s are, respectively, the volume fractions of free polymer and free colloid.

To determine the effect of the presence of the adhered colloids on the micellization properties, in the following we shall focus on the behavior of the function,

$$\begin{aligned} \Omega(m, p) &= \ln \frac{c(0, 1)}{c(m, p)} = \\ &= -(p-1) \ln(c(0, 1)v) - m \ln(c_f v_s) + F^*(m, p) - pF^*(0, 1) \end{aligned} \quad (59)$$

whose minima coincide with the maxima of $c(m, p)$ and, therefore, gives us the average size of the micelle. Here $F^*(m, p) \equiv F(m, p) - f_{ref}$ for any $p \leq 1$ and we consider no energy associated with colloids.

The convenience of this function is the possibility of naturally defining the critical aggregation concentration (cac), i.e., when the concentration of unimers and aggregates is of the same order, this potential is close to 0, while in the absence of the aggregation $\Omega(m, p)$ goes to infinity. For convenience, we analyze $\Omega(m, p)$ as a function of p for fixed m/p , to see how the presence of the adhered colloids change the properties of the "renormalized" block copolymer with m colloids per branch. In Figure 7 we make this analysis for different values of m/p . As we see the presence of adhered colloids induces the micellization and the growth of the micelles as m/p increased.

We have focused our analysis on the regime where colloids are rather scarce along the polymer chains and the polymer concentration remains small in the associated micelles.

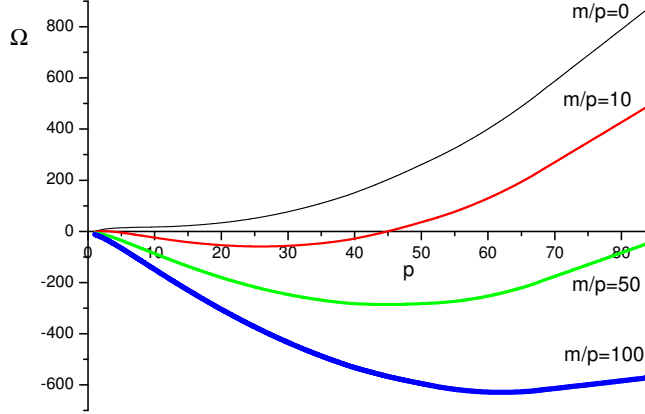


FIG. 7. Variation of $\Omega(m, p)$ as a function of p for different values of m/p . c_f has been set to e^{-10} and $c(0, 1)$, to e^{-30} , $\gamma = 0.7$, $L_c = 50$ and $L = 1000$. Parameters $y \equiv e^{-\varepsilon/kT} \Delta^{\sigma_4 - d\nu + 1} = 25$ and $\alpha \equiv \Delta/L = 10^{-4}$. Notice that for $c(0, 1)$ is below the CMC in the absence of colloids. The presence of colloids favors the micellization as well as the formation of larger aggregates as larger is m/p .

Under these conditions the obtained micelle coronas are in the critical excluded volume regime and the bare interaction between effective monomers (sensitive to the presence of adsorbed colloids) is unimportant. Association is then favored by the effective shortening of the arms. However, at least close to the (small) core of the micelle, there may exist a region where the polymer is in the mean-field regime and therefore be sensitive to the bare magnitude of the excluded volume interaction. The effect of colloids on micellization then may be inverted there, that is, that colloid adhesion does not favor micellization. This regime deserves further consideration, although it lies beyond the scope of this work. Finally, if the chains are heavily loaded in colloids and lose flexibility the excluded volume interaction drops and micellization is then favored by the colloids.

V. CONCLUSIONS

A scaling theory is constructed aiming at the study of the conformations of hydrophilic polymers interacting with small colloidal particles that can reversibly stick onto a polymer backbone. Different geometries have been considered, namely linear polymer chains, star polymers, as well as coronas of block copolymer micelles. Unlike related analyses, we have consistently taken into account the integration of the position of the colloid over the chain

backbone, due to the reversible adhesion of the former onto the polymer.

We find that small colloids adhered to a given polymer induce formation of independent loops of minimal size on each colloid, which can slide along the chain backbone, thus increasing the entropy gain in comparison with static loops of large size. This result is independent of the geometry of the polymer as well as of the nature of the interactions. The sliding degree of freedom of such small loops provides the system with an additional entropic contribution proportional to the length of the polymeric branch. More complex structures such as combined loops, ailed loops, or cactus-like structures are not favorable because of the lack of such a sliding degree of freedom. This contribution has been disregarded in previous analyses in similar systems that rely on the scaling of networks of fixed topology. This is one of the main results of this work.

We have applied these concepts to the equilibrium between colloids and star polymers finding that the saturation of the polymer by the colloids is a crossover process, rather than a phase transition, except for the case of a star with infinitely long arms, where the crossover turns into higher order phase transition in the sense of Ehrenfest, that is, with a finite discontinuity in the third derivative of the free energy. Moreover, the analysis of the micellization problem in the presence of colloids agrees well with the observed experimental fact that the adhesion of colloids favors both, the micellization process, as well as the growth of larger micelles.

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Appendix A: Ailed loop

To illustrate this fact, we can for example calculate the partition function of ailed loops created by the presence of two stickers in the chain, as shown in Figure 3. Similar structures occur in knots formed by slip link contacts³⁶.

Denoting by a the length of the common section of the two ailed loops, whose total sizes

are n_1 and n_2 respectively, and l is the size of the shortest tail, we can write the partition function as $Z \sim a^u n_1^{x_1} n_2^{x_2} l^y (N - l - n_1 - n_2 - a)^z$.

Without loss of generality we choose $n_1 < n_2$, since the loops are symmetrical. In analogy with the previous case it can be shown that the configurations with the loops fixed at a free end, when the short tail satisfies $l < n_1 < n_2$ are subdominant. Then, we consider $n_1 < n_2 < l$. If the common section is small, $a < n_1 < n_2 < l$ we can fix the exponents. If all segments are of the same order of magnitude and comparable to the total size of the chain, one has

$$u + x_1 + x_2 + y + z = 2\sigma_1 + 2\sigma_4 - 2d\nu \quad (\text{A1})$$

If the size of the common segment decreases to one single monomer, $a \rightarrow 1$,

$$x_1 + x_2 + y + z = 2\sigma_1 + \sigma_6 - 2d\nu \quad (\text{A2})$$

If one loop is negligibly small, $a < n_1 \rightarrow 1$, then

$$x_2 + y + z = 2\sigma_1 + \sigma_4 - d\nu \quad (\text{A3})$$

When both loops are vanishing, $a < n_1 < n_2 \rightarrow 1$,

$$y + z = 2\sigma_1 \quad (\text{A4})$$

And, finally, small tail is vanishing,

$$z = 2\sigma_1 \quad (\text{A5})$$

From these equations all exponents can be calculated and the total partition function takes this form

$$Z \sim \int_0^{N/2} dl \int_0^l dn_2 n_2^{\sigma_4 - d\nu} \int_0^{n_2} dn_1 n_1^{\sigma_6 - \sigma_4 - d\nu} \times \int_0^{n_1} da a^{2\sigma_4 - \sigma_6} (N - l - n_1 - n_2 - a)^{2\sigma_1} \quad (\text{A6})$$

After integration, we find

$$Z \sim \Delta^{2(\sigma_4 - d\nu) + 3} N^{2\sigma_1} N \quad (\text{A7})$$

The same scaling is obtained if one considers the other two possibilities, namely, $n_1 < n_2 < a < l$ and $n_1 < a < n_2 < l$ and we have omitted its explicit calculation. As we have seen, the entropy favors the smaller size the possible for the loops. For this particular case this is obtained if both loops tend to shrink to its minimal possible size determined by the cut-off Δ . However since by construction loops are ailed, they are forced to move together along the chain backbone, therefore its entropy is a factor $1/N$ smaller than if they could independently move. This kind of reasoning can be extended to more complex topologies with the same result.

If the sliding link is formed by small associating colloidal particles that can attach and detach from the chain at any point, the formation of individual loops moving separately along the chain is more favorable compared to such combined loops with common segments. Using the same arguments one can see that the partition function of individual loops (17) dominates any other structures with the same number of stickers (combined loops, cactus structures of loops growing on top of each other, etc.).

Appendix B: Calculation of the entropy of the micelles

Self-assembly of polymers into finite size micelles is accompanied by the entropy changes due to the confinement of the polymers assembled into the micelle, which moves as a single object. Here, we estimate the entropic contribution due to this confinement, which involves the integration of the kinetic degrees of freedom, as well as the translational degree of freedom of the polymers as a whole. We recall that the conformation degrees of freedom have been explicitly considered in section II. We are implicitly considering micellization as a two-state situation in which polymers are either free or aggregated into a micelle containing p polymers.

First, we calculate the entropy change due to the association of the p polymers into a micelle in a system containing n of such micelles, to later introduce the effect of the presence of m stickers in each of them. Therefore, the partition function of n non-interacting micelles comprised of p undiscernable polymers, each of length N , is written as

$$Z = \frac{1}{n!} \left[\frac{1}{p!} \int \frac{d\vec{p}_1 \dots d\vec{p}_{Np}}{(2\pi\hbar)^{3pN}} \prod_i^{pN} \exp\left(-\frac{\vec{p}_i^2}{2m_p kT}\right) \times \int d\vec{r}_1 \dots d\vec{r}_p \exp\left(-\frac{U}{kT}\right) \right]^n \quad (\text{B1})$$

where m_p is the mass of a monomer, U is the interaction potential between polymers forming the micelle (undefined). The integration is over all positions of the monomers r , and their momenta p . The micelles are distinguishable only by their composition. We recall that the integration over the translational degrees of freedom is constrained to the polymers to move together as an aggregate, thus the separation between any pair of monomers does not have to exceed the overall size of the aggregate.

Equation (B1) can be rewritten in terms of the partition function of a single micelle of p polymers, Z_p , according to $Z = \frac{1}{n!} [Z_p]^n$, where Z_p is written as

$$Z_p = \frac{1}{p!} \int \frac{d\vec{p}_1 \dots d\vec{p}_{Np}}{(2\pi\hbar)^{3pN}} \prod_i^{pN} \exp\left(-\frac{\vec{p}_i^2}{2m_p kT}\right) \int d\vec{r}_1 \dots d\vec{r}_p \exp\left(-\frac{U}{kT}\right) \quad (\text{B2})$$

The momentum integral can be readily calculated to give a term inversely proportional to Λ_p^{3pN} , where Λ_p is the de Broglie's length of the monomer (thus, independent of N) $\Lambda_p^2 = \hbar^2/(2\pi m_p kT)$, and h , Planck's constant. In the spatial integration we will separate three contributions, namely, the overall translation of the aggregate, related to the center of mass motion, the relative motion of the polymers inside the aggregate, together with the displacement of the monomers of every polymer. The latter gives a contribution proportional to $l_p^{3(N-1)}$ per chain, where l_p is a length of the order of the radius of gyration of the chain, which we will consider a molecular parameter. This contribution has effectively accounted for in the free energy term of the micelle that we have previously calculated (cf. sec. II). Thus, due to the fact that in sec. II the entropy terms are given in a dimensionless form, the factor $l_p^{3(N-1)}$ simply provides the appropriate dimensionality of the expression. As far as the second contribution is concerned, the integration is limited to a distance between any pair of polymers of the order of the size of the aggregate, due to our initial hypothesis of the two-state system (free and confined), and the description that we are doing here of the precisely confined state. Therefore, this second contribution yields a term proportional to V_{agg}^{p-1} , where V_{agg} stands for the volume of the aggregate. The remaining integration over the

position of the center of mass of the aggregate itself yields one additional factor proportional to the overall volume V of the system. Therefore, the final result reads

$$Z_p \sim \frac{1}{p! \Lambda_p^{3pN}} V V_{agg}^{p-1} l_p^{3p(N-1)} \quad (\text{B3})$$

Hence, we can write this entropic contribution to the free energy of the aggregate as

$$\frac{F}{kT} = -\ln Z \sim n \ln \left[\frac{n}{V e} \lambda^3 \right] + n(p-1) \ln \left[\frac{p}{V_{agg} e} \lambda^3 \right] - n \ln \frac{p}{e} \quad (\text{B4})$$

where $\lambda \equiv \Lambda_p^N / l_p^{N-1}$ summarizes only molecular parameters. The first term is for the contribution of a ideal solution of micelles. The second and the third terms stand for the entropy penalty derived from keeping together p polymers into an aggregate. The third term is subdominant in the limit $p \gg 1$. If $p = 1$ this expression should recover the free energy of a dilute solution of independent polymers. Thus, the last term, in addition, should be regarded as an artifact of the distinction we have made between polymers inside the aggregate and outside the aggregate. By consistency, the last term should be dropped to match that mentioned limit, provided that in the more interesting situation $p \gg 1$ is subdominant. Notice that the calculations done in sec. II take into account the entropy due to the conformational changes of a system with p arms, while here we are calculating the entropy penalty of putting these p arms together into an aggregate, understanding that the aggregation process is a physical process. Therefore, V_{agg} should be regarded as the volume of the core of the micelle and not that of the whole aggregate, including the corona.

Similar arguments have been used in Refs.^{37,38} to derive the entropy penalty for the formation of the micelle, obtaining an expression similar to the second term in our eq. (B4). The main difference comes from the presence in our expression of the λ^3 term. Therefore, the entropic contribution of Ref. 38 should be regarded as with respect to a reference state. Effectively, let us introduce a volume V_0 , where $V_0 \equiv Nv$, v being the volume of the monomer, into the logarithmic term, and subtract it afterwards. The free energy can be written as

$$\frac{F}{kT} = n \ln \left[\frac{n}{eV} V_0 \right] + n(p-1) \ln \left[\frac{p}{eV_{agg}} V_0 \right] - np \frac{f_{ref}}{kT} \quad (\text{B5})$$

where f_{ref} is the free energy per polymer in a reference state, defined as

$$\frac{f_{ref}}{kT} = \ln \frac{V_0}{\lambda^3} \quad (\text{B6})$$

Eq. (B5) is exactly the same expression as in Ref. 37.

In the case of the colloids, the situation is different, for the entropy of the adhered colloid has already taken into account in the derivation of $Z(m, p)$. Notice that this expression accounts for the energetic contribution $\exp(-\varepsilon m)$, the translational entropy due to the colloid motion along the chain backbone, as well as the indiscernibility of the colloids. Therefore, we are only facing the contribution due to the chain aggregation.

Finally, for convenience, we introduce the volume of the monomer v instead of V_0 into the expression (B4). Then, eq. B4 can be rewritten as

$$\frac{F}{kT} = -\ln Z \sim n \ln \left[\frac{n}{Ve} v \right] + n(p-1) \ln \left[\frac{p}{V_{agg}e} v \right] - np f_{ref}(T) \quad (\text{B7})$$

where $f_{ref}(T) \equiv \ln v/\lambda^3$ which is only dependent on the temperature and molecular parameters, and, in addition, is independent of the size of the polymer. We use this function in the construction of the free energy in eq. (56) for the systems of micelles of different size and number of colloids in equilibrium.

Therefore, from this expression we can identify that the contribution that yields F_{conf} is given by the second term in B7, that is

$$nF_{conf}/kT = n(p-1) \ln \left[\frac{p}{V_{agg}e} v \right] \quad (\text{B8})$$

As it has been mentioned, the other contributions are explicitly accounted for in the proposed expression for the free energy, eq. (56).

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